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MODEL FOR STUDYING CALORIMETRY WITH PROGRAMMED TEMPERATURE FOLLOWED BY ISOTHERMAL HEATING. CALCULATION OF HEAT FLUX AND PROFILES OF TEMPERATURE WITH CURE REACTION OF HIGH ENTHALPY

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ABSTRACT

In our previous works concerned with rubber sheets, profiles of temperature and state of cure developed through the thickness of the sheets were described and calculated by using a model. This model has been applied to the study of the calorimetry method working with a temperature programme followed by heating under isothermal conditions. The model takes into account heat transfer by conduction and the kinetics of heat evolved by the cure reaction, and it uses an explicit numerical method with finite differences. The heat flux transferred from the sample surface to the calorimeter cell is determined as a function of time, and compared at the same time with the profiles of temperature and state of cure obtained through the sample. The internal heat generated by the cure reaction is responsible for high gradients of temperature through the sample. A comparison between this calorimetry technique and the classical one under isothermal conditions is made by taking into account all these facts.

INTRODUCTION

Numerous thermoanalytical techniques are used for determining cure processes. Some of them, such as differential scanning calorimetry (DSC) and differential calorimetry (DC), are well known. In these techniques, enthalpy changes accompanying chemical events in the system are monitored either as a function of temperature as the sample is heated at a known linear rate (DSC) or as a function of time, the calorimeter being held at constant temperature (DC). The detailed kinetics of the enthalpy profiles are possible for studying simple cure reactions.

These two techniques have some advantages and drawbacks, when compared. For instance, one source of error arises in these two techniques from heat transfer between the sample and the calorimeter cell [1]. Because of the internal heating arising from the exothermic reaction and the sample exhibiting a low heat transfer, the applied and measured temperatures are those of

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the calorimeter and not the local temperatures in the sample during the cure. Moreover, profiles of temperature are developed through the sample studied, with resulting profiles of state of cure (SOC) [2,3]. Because of all these facts, research on heat flux–time curves obtained in the calorimeter cell is ambiguous and a study of the kinetics of the cure is clearly not feasible. This drawback is particularly apparent in the DC techniques when high temperatures are used. Another inconvenience for the above technique results from the lack of information at the beginning of the operation, after the sample is dropped into the calorimeter. For about 1 min, if samples of 100–200 mg are used [4], and in any case for more than 20 s, no information can be obtained, because of the high endothermic effect due to the very strong heating of the sample.

In order to avoid the drawbacks of the DC technique, another application of the DC technique was described [4,5], combining both the DC and DSC techniques. This method consists of a programmation of the temperature of the calorimeter and sample from room temperature to the constant temperature, followed by isothermal heating. This paper provides detailed information on this method.

To afford a further insight into the nature of the heating and cure kinetics obtained through the sample, the heat flux evolved through the sample–calorimeter interface is calculated as a function of time, as well as the profiles of temperature and state of cure developed in the sample at the same time. In previous work, we pointed out that these profiles of temperature and state of cure can be predicted by calculation when developed through rubber sheets [5,6] or cubic samples [7], if the kinetics of the overall cure reaction are known as well as heat transfer parameters. In the present work, this mathematical model has been applied to the study of the heating and cure process in a cylindrical sample submitted to heating in a calorimeter according to the DSC–DC technique. The extent of the cure reaction is determined by the balance of internal heat generation from the reaction, conduction through the mass and the calorimeter–sample interface. This problem is solved by applying a numerical method with fine differences in the case of the cylindrical sample. Although the cure of epoxide resin is a complex chemical process, the kinetics of heat evolved by the overall reaction are described by a single equation with a constant activation energy.

THEORETICAL

Mathematical treatment

Several assumptions are made for the present study:

(1) a cylindrical sample is used, with a diameter of 6 mm;

(2) heat transfer is radial, and studied through the cross-section of the sample, circular in shape;

(3) heat is transferred only by conduction through the epoxide resin, and through the calorimeter sample interface;

(4) the quality of contact between the sample and calorimeter is considered;

(5) the kinetics of the overall reaction follow a single reaction with a constant activation energy.

From the above assumptions, the equation governing radial heat conduction through the cross-section of the sample is reduced as follows

$$\rho C\frac{\partial T}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda\frac{\partial T}{\partial r}\right)+\rho\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

The rate of the overall reaction of cure is given by the single equation

$$\frac{\mathrm{d}Q(r,t)}{\mathrm{d}t}=K_0(Q_\infty-Q_{r,t})\exp-\frac{E}{RT} \tag{2}$$

where $Q_{r,t}$ is the heat of reaction evolved up to the time t at the position r in the cross-section.

The temperature of the calorimeter is varied according to this scheme: programmation from room temperature to the constant value, followed by isothermal heating

$$T_t=20+bt \tag{3}$$

where T_t is the cell temperature, and b is the heating rate.

Initial and boundary conditions in the sample are as follows

$t=0$	$0\leqslant r\leqslant R_s$	$T=T_r$	sample space	(4)
$t>0$	$r\geqslant R_s$	$T=T_m$	oven space	(5)
	$0\leqslant r<R_s$	$T=T_{r,t}$	sample space	

Numerical analysis

Equations (1) and (2) cannot be solved in the present case by a mathematical treatment, because of the internal heating due to the cure reaction. An explicit numerical analysis is used.

By considering in the cross-section the successive circles with radii $r-\Delta r$, r, $r+\Delta r$ (Δr being a constant increment) the balance of heat exchange for the ring between $r-\Delta r/2$ and $r+\Delta r/2$ is reduced to the following equation during the increment of time Δt

$$T_{i+1,r}=\frac{1}{M}\left[T_{i,r+\Delta r}+(M-2)T_r+T_{r-\Delta r}\right]+\frac{\Delta r}{2Mr}\left[T_{i,r+\Delta r}-T_{i,r-\Delta r}\right]+\frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{6}$$

For determining the value of the temperature in the middle of the cross-section, eqn. (7) must be used

$$T_{i+1,0} = \frac{4}{M}(T_{i,\Delta r} - T_{i,0}) + \frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \qquad (7)$$

where $T_{i+1,r}$ is the temperature in the ring between $r - \Delta r/2$ and $r + \Delta r/2$ at time t.

The dimensionless modulus M is related to the increments of time and space

$$M = \frac{(\Delta r)^2}{\Delta t}/\alpha_s \qquad (8)$$

where α_s is the diffusivity of the sample.

A particular treatment is necessary to describe the heat transfer through the calorimeter–holder interface.

$$T_{i+1,R_s} = \frac{H}{1+H}T_{i,m} + \frac{1}{1+H}T_{i,R_1} \qquad (9)$$

$T_{i,\mathrm{m}}$ is the temperature of the calorimeter expressed by eqn. (3), and T_{i,R_s} the temperature at time i and on the surface of the holder.

The coefficient H is calculated with the equation

$$H = \left(\frac{\alpha_\mathrm{m}}{\alpha_\mathrm{s}}\right)^{1/2}\frac{\lambda_\mathrm{s}}{\lambda_\mathrm{m}} \qquad (10)$$

where α is the heat diffusivity for mold and sample, and λ is the thermal conductivity.

The state of cure is described in this paper as the heat of cure evolved up to time t as the ratio of the total heat of cure. The heat of cure evolved up to time t is obtained from the following equations

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{i+1}\Delta t = Q_{i+1} - Q_i = (Q_\infty - Q_i)K_0 \exp -\frac{E}{RT_i}\Delta t \qquad (11)$$

$$Q_i = \sum_{i=0}^{i}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i\Delta t \qquad \text{and } Q_0 = 0 \qquad (12)$$

The heat flux (HF) transferred from the sample to the calorimeter must be calculated in this paper. It is considered as exothermic when the temperature of the sample is higher than that of the calorimeter, and endothermic in the opposite case. The heat flux is obtained with the single equation

$$\mathrm{HF} = \lambda_\mathrm{s}\frac{T_{R_s} - T_{R_s-\Delta r}}{\Delta r} \qquad (13)$$

EXPERIMENTAL

Calorimeter

The sample (100–200 mg) to be studied is put into an aluminium holder of 6 mm diameter. The holder is placed in the calorimetric block whose temperature is controlled. A heat-flux detector consisting of thermocouples is in contact with the holder so that the temperature of the holder face is as close as possible to that of the block. The signal emitted by the heat-flux detector is proportional to the heat transferred per unit time. The signal is considered as exothermic when heat is transferred from the holder to the detector. As the sample is cylindrical in shape, it is surrounded by the detector and no heat flux is lost. The DSC 111 (Setaram) is used through all the work, but the results obtained could be useful for any other apparatus by taking into account the dimensions and size of the holder.

The operation conditions are as follows: programmation of the temperature for the calorimeter from room temperature to the constant temperature, followed by heating under isothermal conditions. The rate of heating is 10°C min^{-1}. The constant temperature ranges from 130 to 150°C.

Materials

An epoxide resin is chosen for this study. The main characteristics of the cure reaction are shown in Table 1.

The enthalpy of reaction, Q_∞, and the heat capacity, C, are measured by calorimetry. The diffusivity, α, is determined by a flash method [8]; in this method, one face of the epoxide resin layer is subjected to a thermal impulse of short duration and the evolution of temperature is recorded on the other face of the layer. The kinetic parameters are determined by microcalorimetry working under isothermal conditions at temperatures ranging from 130 to 150°C. The values cited are in agreement with some of the values found in earlier literature [9–11].

Calculation

The values chosen for the increment of space and the resulting increment of time are shown in Table 2, by taking care to keep the modulus higher than 2. A value of 5 for M allows the calculation to converge.

TABLE 1

Cure characteristics of the epoxide resin

$Q_\infty = 65$ cal g^{-1}; $E = 15000$ cal mol^{-1}; $K_0 = 3 \times 10^5\ \text{s}^{-1}$;
$\alpha = 25 \times 10^{-4}\ \text{cm}^3\ \text{s}^{-1}$; $C = 0.32$ cal $\text{g}^{-1}\ \text{deg}^{-1}$; $\lambda = 10^{-3}$ cal $\text{cm}^{-1}\ \text{s}^{-1}\ \text{deg}^{-1}$;
order $n = 1$

TABLE 2

Values chosen for computerization

$R_s = 0.25$ cm; $\Delta r = 0.025$ cm; $\Delta t = 0.05$ s; $M = 5$; $H = 1$–20

As it is difficult to obtain at the present time a definite value for the coefficient H described in eqn. (10), we have tested several values ranging from 1 to 20. A value of 1 corresponds to the quality of the transfer obtained between epoxide resin and the resin itself; the value of 20 is attained for the interface metal–epoxide resin when they are in good contact.

RESULTS

Several parameters are found of interest and their effect on heat flux–time curves are especially studied in this work.

(i) The value of H expressed in eqn. (10) is directly related to the coefficient of heat transfer between two different solids [12]; here, it defines the quality of contact between the holder and calorimetry vessel, as shown above.

(ii) The profile of temperature and state of cure, obtained at the same time as heat flux–time curves. This is a result worth pointing out in this paper.

(iii) The classical effect of temperature in the calorimeter.

(i) Effect of the quality of contact (H) *on calculated and experimental curves obtained by calorimetry*

Figure 1 illustrates a typical DSC–DC curve for the cure of an epoxide resin. For the example illustrated, the temperature of the calorimeter is programmed from 20 to 150°C with a constant heating rate of 10°C min^{-1}. At the time of 13 min, the temperature is maintained at the constant value of 150°C. For the example illustrated, cure reactions are initiated at about 90°C and a maximum in the rate of enthalpy evolution is observed at about 150°C, just at the end of the heating programme. After cure in the calorimeter, the sample is usually cooled and rescanned under the same conditions, to give the temperature dependence of the specific heat of the cured product as formed after the initial experiment. In general, the rescan curve can be superimposed on the initial curve to give the baseline which could be observed in the absence of cure. In the present work, the simulation of cure is obtained by calculating the heat flux as a function of time with the value of 3×10^5 s^{-1} for the rate constant; the baseline is obtained in the normal way by taking 0 for the rate constant. In our calculations, we have not taken into account the dependence on temperature of the specific heat of materials. Thus, this is the only difference which can be appreciated between calculated

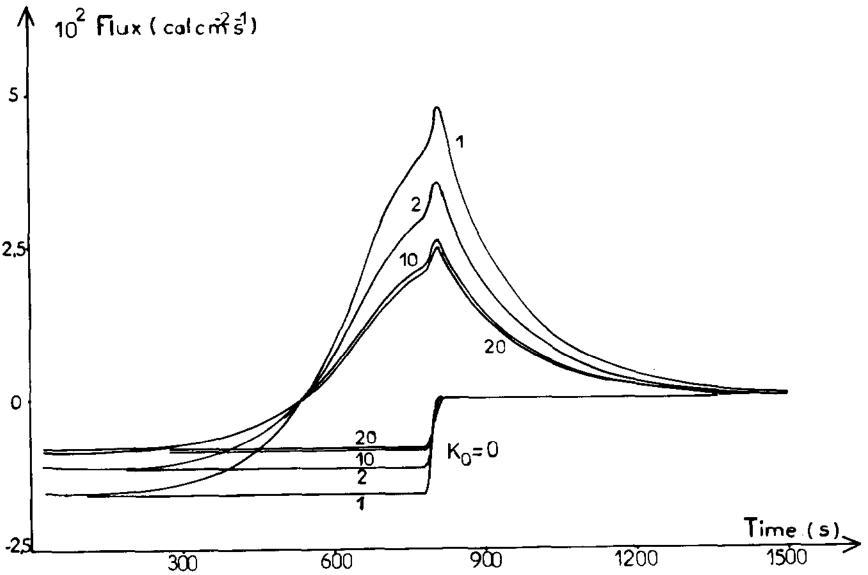

Fig. 1. Effect of H on heat flux–time curves at 150°C. $K_0 = 3\times10^5$ s^{-1}, $K_0 = 0$.

and experimental heat flux–time curves. Of course, the two curves calculated for $K_0 = 3 \times 10^5$ s^{-1} and 0 are concurrent at times of about 25 min.

As shown in Fig. 1, heat flux–time curves undergo a transformation when the coefficient H is varied. This new result is very important for the calorimetry technique, but it may temperated by the following two facts.

(a) All the curves obtained with a different value for H are similar, and this is a point worth mentioning, the similarity ratio is the same at any point located along the curves. As shown in Table 3, the ratio of similarity depends only on the value given to the coefficient H, so all the curves obtained with four different values of H exhibit the same temperature for cure initiation, and pass through a maximum at the same temperature and time.

In Table 3, heat flux values are calculated for different values of H and expressed as a function of the heat flux obtained for $H = 20$.

Another fact worth mentioning is the constant value of the similarity ratio with the temperature of the calorimeter.

TABLE 3

Effect of H on similarity ratio (r_s) of heat flux–time curves

Calorimeter temperature	=140°C				150°C		
	$H=1$	2	5	10	1	2	10
HF_{max}	1.93	1.44	1.16	1.06	1.95	1.45	1.06
$\frac{1}{2}HF_{max}$	1.93	1.44	1.16	1.06	1.95	1.45	1.06
$\frac{1}{4}HF_{max}$	1.93	1.44	1.16	1.06	1.95	1.45	1.06

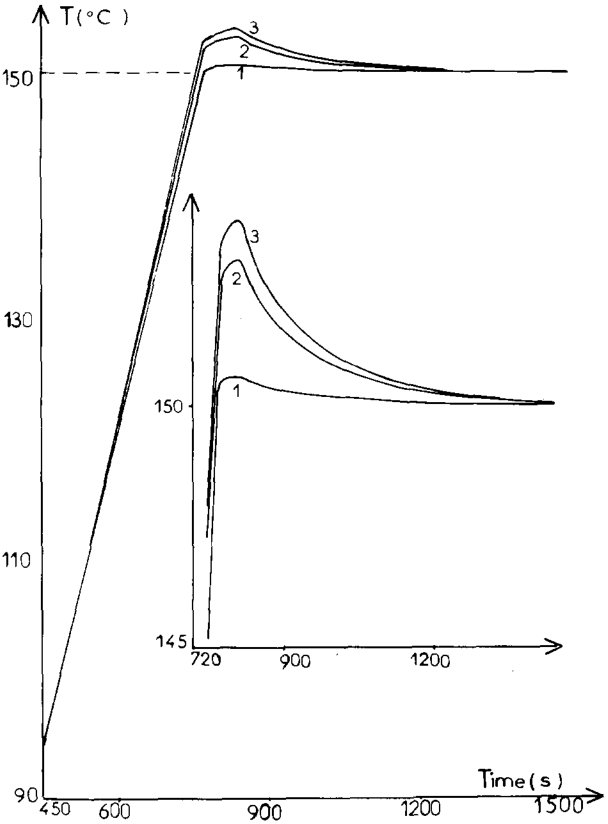

Fig. 2. Temperature vs. time in different places through the sample: (1) face; (2) $r = R_s/2$; (3) middle; $H = 1$; 150°C; $K_0 = 3 \times 10^5$ s^{-1}; 0.6 cm.

(b) The value obtained for the coefficient H has a noticeable effect on the sensitivity of the heat flux of cure reaction. The lower the value of H, the higher the sensitivity measured for the heat flux. However, this effect of H on sensitivity is important only for low value of H, and becomes of low significance when H ranges from 10 to 20.

(ii) Determination of profiles of temperature and state of cure through the sample

The effect of the value given to the coefficient H on the profiles of temperature can be appreciated by comparing Fig. 2 for $H = 1$ and Fig. 4 for $H = 20$. These profiles of temperature developed as a function of time are shown at three positions in the sample: (1) on the sample surface, (3) in the middle of the cylindrical sample, and (2) for $r = R_s/2$. A slight difference can only be seen for these profiles: $\frac{1}{2}$ degree for the value of the maximum of temperature obtained at the three above positions chosen through the sample; the time at which the maximum is apprehended depends noticeably on the value of H.

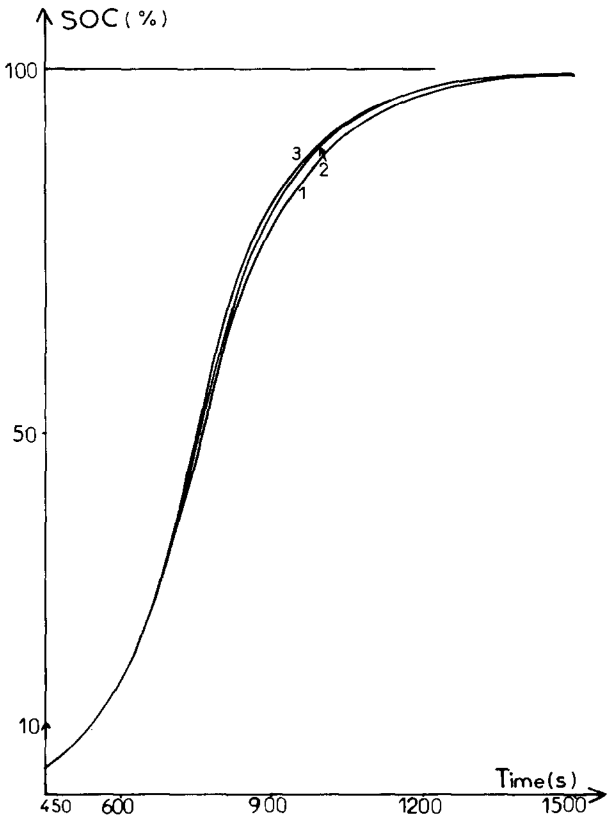

Fig. 3. SOC vs. time in different places through the sample: (1) face; (2) $r = R_s/2$; (3) middle; $H = 1$; 150°C.

The most important result is the variation in the temperature, not only with time but also through the sample. Thus, the problem for determining kinetic parameters of interest for cure reactions becomes rather complicated.

The effect of the value of the coefficient H on the profiles of state of cure can be seen by comparing Fig. 3 for $H = 1$ and Fig. 5 for $H = 20$. These profiles are developed with time at the same three positions in the sample. All these curves are approximately similar in shape and position.

Of course, the simultaneous knowledge about the rate of cure reaction expressed by heat flux–time curves, at different times and positions through the sample, affords a further insight into the nature of cure reactions obtained with calorimetry.

(iii) Effect of the temperature of the calorimeter

In the present work, the mathematical model has been applied to the study of the classical effect of the calorimeter temperature on the rate of cure reaction (heat flux). The model provides the possibility of precisely determin-

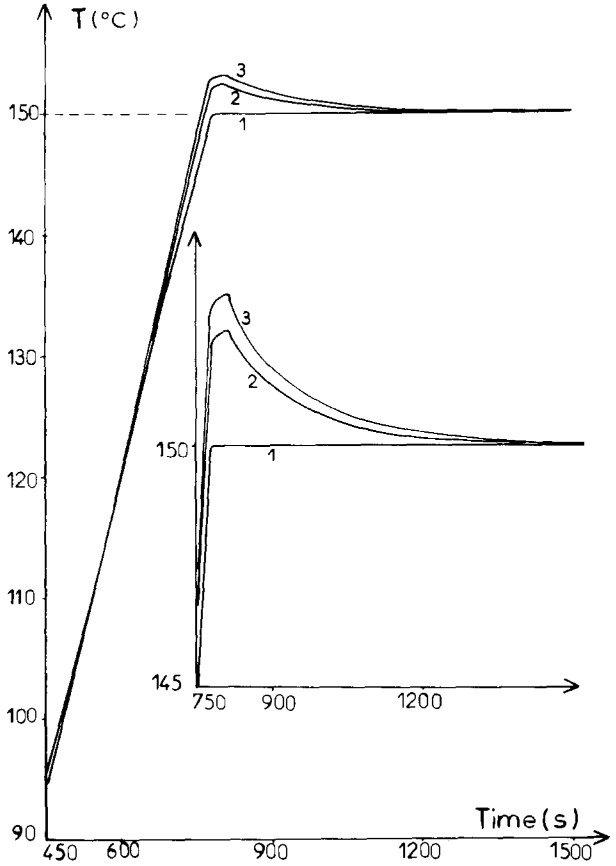

Fig. 4. Temperature vs. time in different places through the sample: (1) face; (2) $r = R_s/2$; (3) middle; $H = 20$; 150°C.

ing this effect on the profiles of temperature developed against time at different places chosen in the sample, as well as on the profiles of state of cure.

The effect of the chosen calorimeter temperature on heat flux produced by the sample can be evaluated by comparing the curves in Fig. 6 drawn at 140°C, in Fig. 7 at 130°C and Fig. 1 at 150°C. This result is classical and well known, and is in agreement with our experimental curves determined under the same conditions.

To gain a fuller insight into this problem, this paper provides detailed information on the profiles of temperature and state of cure obtained as a function of time for the different temperatures of the calorimeter given above. The profiles of temperature calculated at the three positions in the sample are drawn against time for the three temperatures in Fig. 8, and the subsequent profiles of state of cure are given in Fig. 9.

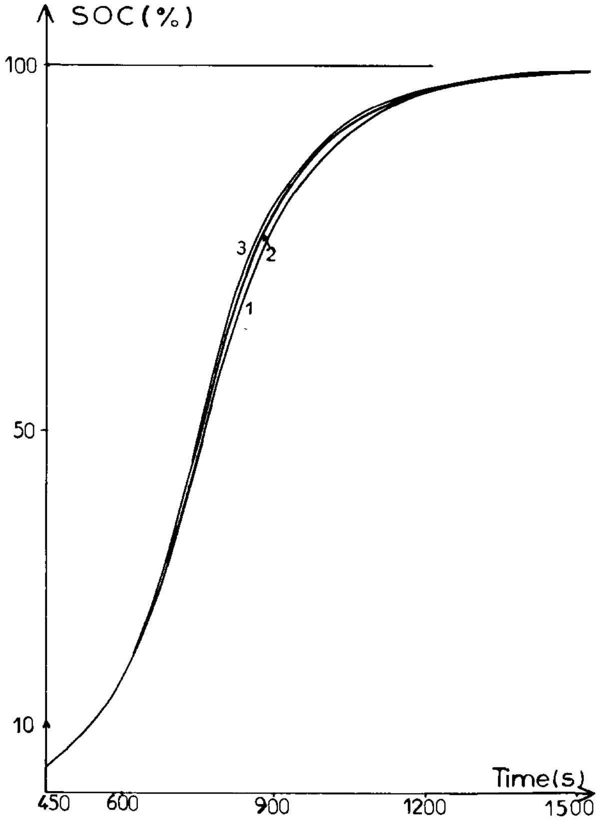

Fig. 5. SOC vs. time in different places through the sample: (1) face; (2) $r = R_s/2$; (3) middle; $H = 20$; 150°C.

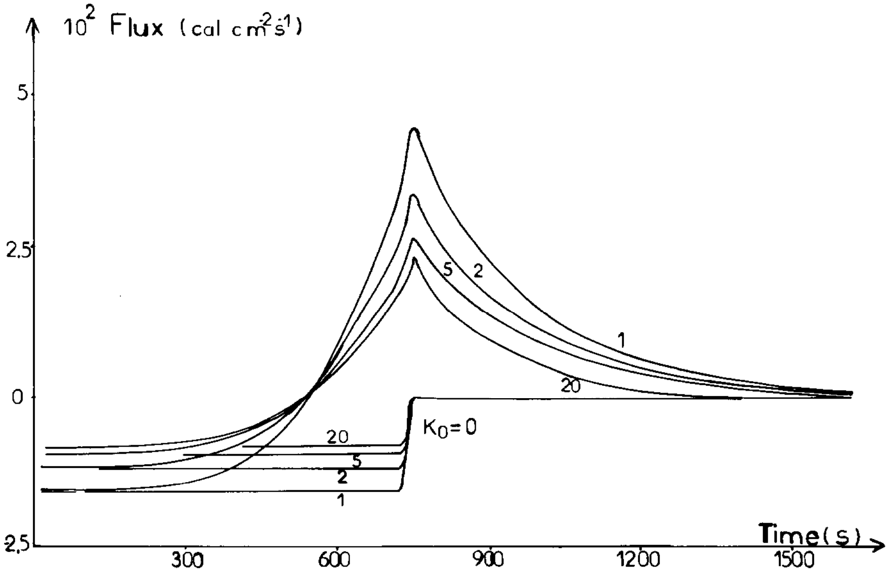

Fig. 6. Heat flux–time curves obtained at 140°C, for different values of H.

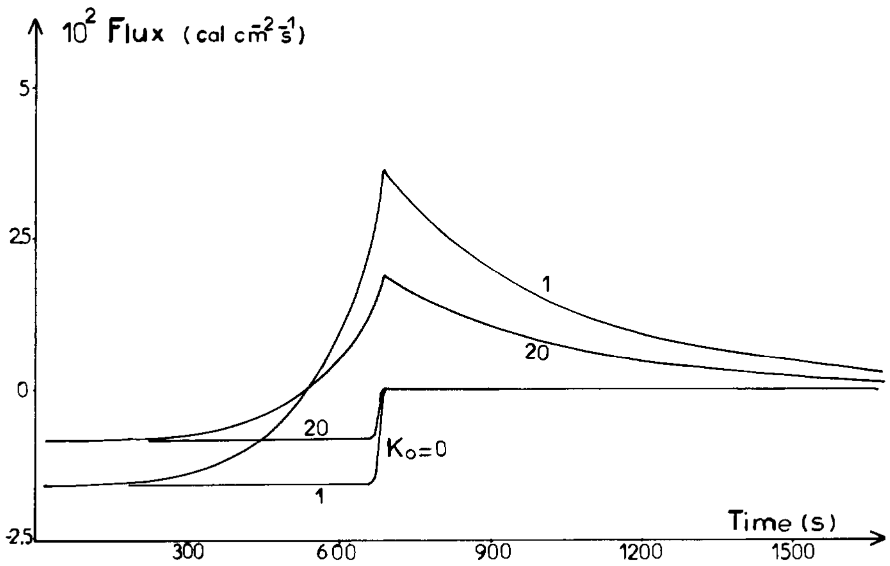

Fig. 7. Heat flux–time curves obtained at 130°C, for different values of *H*.

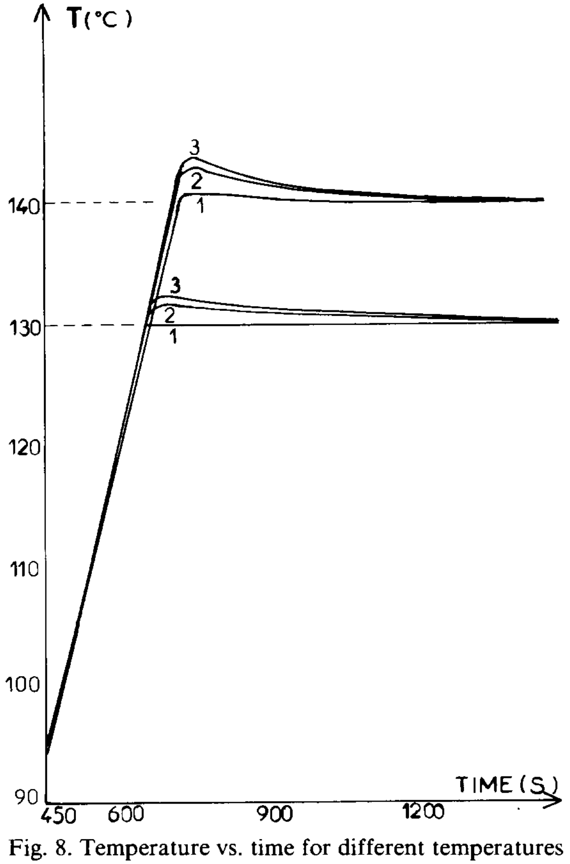

Fig. 8. Temperature vs. time for different temperatures in calorimeter: 130–140°C; $H = 1$; (1) face; (2) $r = R_s/2$; (3) middle.

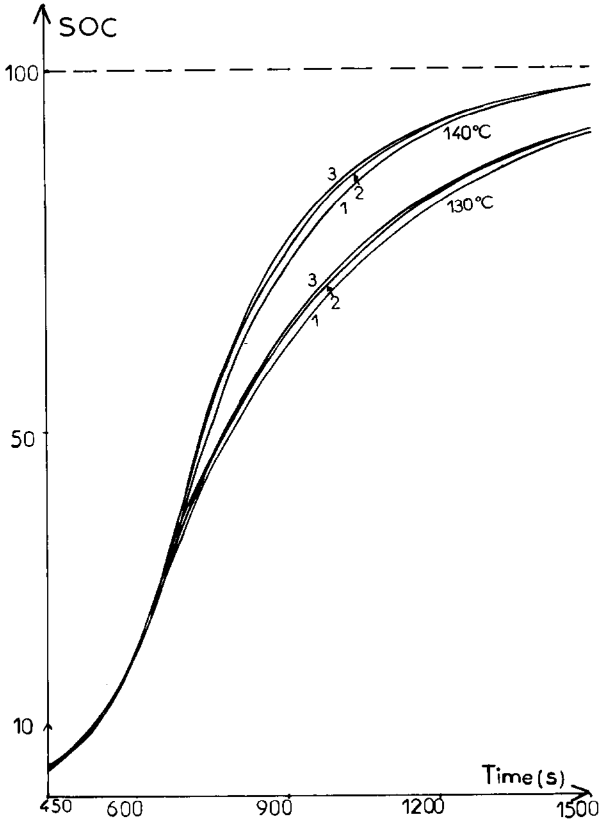

Fig. 9. SOC vs. time for different temperatures in calorimeter: 130–140°C; $H = 1$; (1) face; (2) $r = R_s/2$; (3) middle.

CONCLUSIONS

The purpose of this paper has been to afford a further insight into the nature of cure reactions developed in epoxide resin samples by calorimetry. The paper has provided detailed information on the profiles of temperature and state of cure obtained as a function of time, as the heat flux emitted through the sample–calorimeter interface is calculated. Comparisons between all these results show that the problem at hand for determining kinetic parameters from heat flux–time curves is not at all easy. The temperature at which the sample is raised in excess of that of the calorimeter is of several degrees, and must be considered for these calculations. The quality of the contact between the epoxide resin and holder, as well as that between the holder and the calorimeter, is also of importance.

The work is progressing, and these basic results will be of interest in order to develop this calorimetry technique and help workers to obtain accurate kinetic parameters for cure reactions of high enthalpy.

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